

Optical properties of MgCNi₃ in the normal state

P. Zheng, J. L. Luo, G. T. Liu, Y. L. Zhang, R. C. Yu, C. Q. Jin, and N. L. Wang*
*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences,
 Beijing 100080, People's Republic of China*

M. Q. Tan

Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

(Received 3 May 2005; published 21 September 2005)

We present the optical reflectance and conductivity spectra for nonoxide antiperovskite superconductor MgCNi₃ at different temperatures. The reflectance drops gradually over a large energy scale up to 33 000 cm⁻¹, with the presence of several wiggles. The reflectance has slight temperature dependence at low frequency but becomes temperature independent at high frequency. The optical conductivity shows a Drude response at low frequencies and four broad absorption features in the frequency range from 600 to 33 000 cm⁻¹. We illustrate that those features can be well understood from the intra- and interband transitions between different components of Ni 3*d* bands which are hybridized with C 2*p* bands. There is a good agreement between our experimental data and the first-principles band structure calculations.

DOI: [10.1103/PhysRevB.72.092509](https://doi.org/10.1103/PhysRevB.72.092509)

PACS number(s): 74.25.Gz, 78.20.-e, 78.30.-j

The discovery of nonoxide superconductor MgCNi₃ has attracted much attention due to the coexistence of ferromagnetic element Ni and superconductivity.¹ MgCNi₃ has the cubic antiperovskite lattice structure with space group $Pm\bar{3}m$, in which eight Mg atoms occupy the cubic corners, while six Ni atoms are at the face-center positions and one C atom is inserted into the body-center position. The lattice parameter a is 3.81 Å.¹ Hall effect,² thermopower, and thermal conductivity³ measurements indicate electron-type conducting carriers in MgCNi₃. A number of experiments including ¹³C NMR measurement below T_c ,⁴ the determination of the upper critical field $H_{c2}(0)$ from the resistance $\rho(T)$ under different magnetic fields,² and the specific heat measurements⁵ show that MgCNi₃ is a conventional superconductor. But band calculations indicate that the Ni 3*d* electrons dominate the density of the states (DOS) near the Fermi level E_F .⁶⁻⁹ Then, the Ni 3*d* electrons are usually considered to take part in the superconducting pairing in MgCNi₃. In such a case, a *s*-wave pairing is unexpected because of the existence of the localized moment of the Ni atom which will break the *s*-wave superconducting pairing.

The relationship between the electronic states of Ni and the superconductivity in MgCNi₃ was intensively studied. All of the known substitutions at the Ni site are found to decrease the superconducting temperature and/or bulk superconducting volume.¹⁰⁻¹² Normal state ¹³C NMR measurement implies the existence of spin fluctuation above 20 K.⁴ The calculated Stoner exchange parameter $S=0.43-0.64$ (Refs. 7 and 13) and the Stoner renormalization is 5.⁸ The value is at the high edge of the paramagnetic region and close to the ferromagnetic region which may lead to ferromagnetic spin fluctuation. Apparently, Ni is related with the superconductivity but its electronic and magnetic properties are different from those in pure fcc Ni. Considering that MgCNi₃ has the isomorphic lattice as the pure Ni, the effect of Mg, C atoms should be important to change the electronic and the magnetic properties of Ni in MgCNi₃. Dugdale and

Jarlborg⁷ studied the effect of Mg, C on MgCNi₃ in comparison with the fcc Ni. Their calculation suggests that for MgCNi₃, both the face-center substitutions of fcc Ni by Mg atoms and the occupation of the C site at the body-center position will make the Fermi level E_F of MgCNi₃ move away from the large DOS peak and make $N(E_F)$ smaller than that of fcc Ni, leading to a decrease of the Stoner factor and a disappearance of the magnetic order. Other theoretical studies show that^{8,13,14} the correlation of Ni 3*d* electrons in MgCNi₃ is not very important like in fcc Ni due to strong hybridization between Ni 3*d* and C 2*p* states.

The optical conductivity has been calculated based on the first principles band structure study.^{15,16} According to the local orbital symmetry of Ni, the Ni 3*d* states should be decomposed into xy , $yz+zx$, x^2-y^2 , and $3z^2-r^2$ components. They contribute to the region from the +1 to -4 eV. The C *p* orbitals are hybridized with Ni *d*, and are located below most of the the Ni *d* states. The partial DOS calculations further indicate that the states very close to E_F are derived by Ni $3d_{yz+zx}$ and $3d_{3z^2-r^2}$ orbitals, which also dominate the chemical bonding between C and ligand Ni atoms. The contributions by Ni $3d_{xy}$ and x^2-y^2 are somewhat away from E_F . The calculated conductivity spectrum at low energy is dominated by intra- and interband transitions among those Ni 3*d* states. The spectrum appears quite different from that of pure fcc Ni which has only two peaks at 0.3 and 1.4 eV below 4 eV at 300 K.¹⁷ But up to now, as far as we know, there is no experimental study on the optical properties of MgCNi₃ compound. In this work, we report our optical reflectance investigation on the MgCNi₃ superconductor from 50 to 46 000 cm⁻¹ at different temperatures. Our study shows that Ni 3*d* bands really dominate the electronic structure near the Fermi level, but the 0.3 and 1.4 eV peaks which is related to the ferromagnetic property of pure fcc Ni disappear in MgCNi₃. A narrow Drude response exists in the low frequency region. There are four interband transitions below 4 eV. The origin of the intra- and interband transitions is discussed.

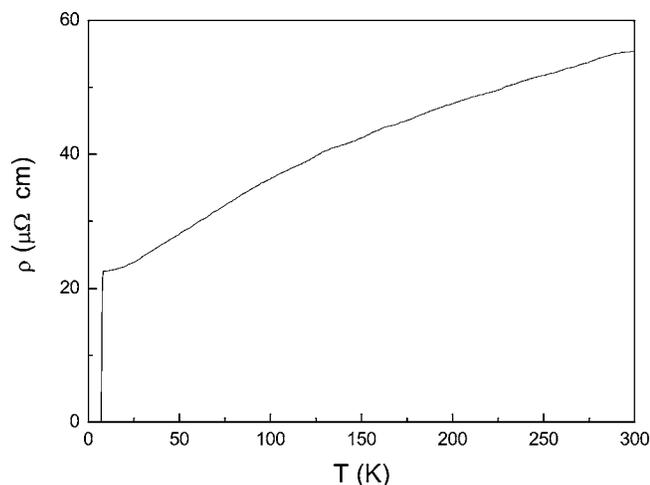


FIG. 1. Temperature dependence of the resistivity of MgCNi_3 .

Because there is no available single crystal of the MgCNi_3 compound, we performed our optical study on a polycrystalline MgCNi_3 sample prepared by conventional solid state reaction followed by post high pressure treatment. A single phase polycrystalline MgCNi_3 compound was first synthesized using solid state reaction as described in Ref. 18. Then, the compound was further treated at 800 °C for 5 min under pressure of 5 GPa. The obtained sample is extremely dense and checked again to be pure phase by x-ray diffraction. A very shiny and metallic bright surface was obtained after fine polishing. Since the material has a cubic structure, optical constants of MgCNi_3 should be isotropic, therefore we can determine its optical constants from the reflectance measurement on such a polycrystalline sample. The frequency-dependent reflectance $R(\omega)$ was measured from 50 to 46 000 cm^{-1} at different temperatures. The measurements below 25 000 cm^{-1} were performed on a Bruker 66 v/s spectrometer. A grating type spectrometer was used for the measurement above 20 000 cm^{-1} . Good agreement is seen in the overlapped frequency region. An *in situ* gold (below 15 000 cm^{-1}) and aluminum (above 15 000 cm^{-1}) overcoating technique was used for the experiment, then the data were corrected for the absolute reflectivity of gold and aluminum. We use Hagen-Rubens relation for the low frequency extrapolation, and a constant extrapolation to 100 000 cm^{-1} followed by a well-known function of ω^{-4} in the higher-energy side.

Figure 1 displays the temperature dependence of the resistivity measured by a standard four-probe method. It shows metallic behavior in the normal state. Its superconducting temperature T_c is 7.8 K and $\Delta T|_{T_c} = 1.7$ K, showing a high quality of our sample. Figure 2 shows the frequency dependent reflectance $R(\omega)$ at 300 K from 50 to 46 000 cm^{-1} . The inset shows the $R(\omega)$ spectra at 300, 180, and 10 K from 50 to 8000 cm^{-1} . $R(\omega)$ at 300, 180, and 10 K cross near 3000 cm^{-1} . The reflectivity of MgCNi_3 monotonically decreases with the frequency up to 33 000 cm^{-1} , showing a typical over-damped characteristic. Several wiggles could be observed in this energy region. Such a shape is roughly similar to the frequency dependence of reflectivity of pure fcc

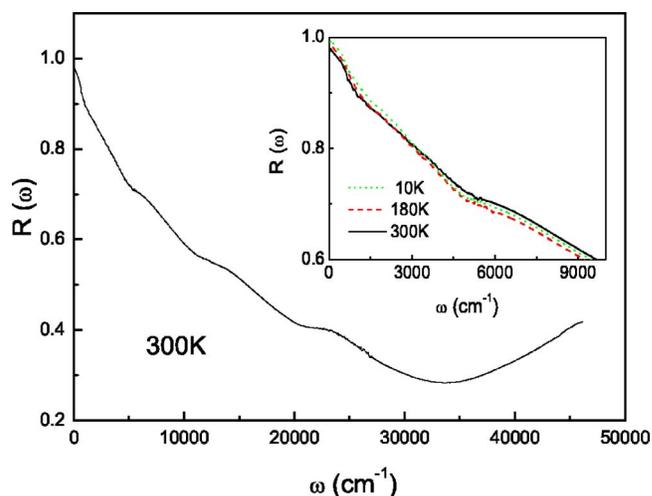


FIG. 2. (Color online) Frequency dependence of reflectivity $R(\omega)$ at 300 K in the frequency region from 50 to 45 000 cm^{-1} . The inset shows the spectra of $R(\omega)$ 300, 180, and 10 K from 50 to 8000 cm^{-1} , respectively.

Ni.¹⁷ As reported, the gradual drop of the reflectivity in this range appears to be a characteristic behavior of most metals like Fe, Co, and Pd in which the d bands play a prominent role.¹⁷ The similarity of optical spectra between MgCNi_3 and pure Ni metal implies that Ni $3d$ bands dominate the electronic structure of MgCNi_3 below 33 000 cm^{-1} and is consistent with the theoretical analysis. However, differences between the two materials are also remarkable especially in high frequency region: (1) In the reflectance spectrum of MgCNi_3 , there are two more broad peaks than pure Ni. (2) The central positions of the other two broad peaks have moved, as we illuminate below.

Figure 3 shows the real part of the optical conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ below 40 000 cm^{-1} at 300, 180, and 10 K. The conductivity at the low-frequency limit $\sigma_1(\omega)$

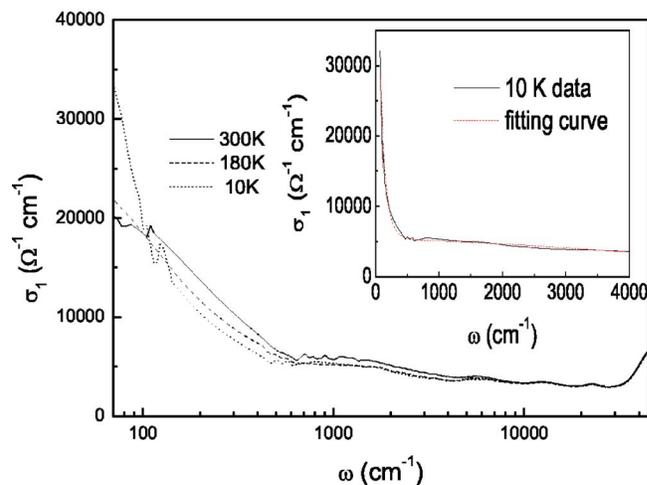


FIG. 3. (Color online) Frequency dependence of the optical conductivity $\sigma_1(\omega)$ at different temperatures. The solid line is for 300 K, the dashed line is for 180 K, and the dotted line is for 10 K. The inset shows the fitting result at 10 K, in which the solid line is the experimental data and the dashed line is the fitting line.

$\approx 20\,000\ \Omega^{-1}\text{cm}^{-1}$, which is close to the value at 300 K deduced from Fig. 1. A Drude response exists in the low frequency region below $600\ \text{cm}^{-1}$. In the frequency region from 600 to $33\,000\ \text{cm}^{-1}$, there are four broad peaks centering at 1300 , 5700 , $12\,700$, and $22\,900\ \text{cm}^{-1}$ (i.e., 0.16 , 0.7 , 1.6 , and $2.84\ \text{eV}$), respectively. The four peaks keep present down to 10 K. The three peaks at high frequency are hardly temperature dependent, while the low frequency peak and the Drude response show slight temperature dependence: The height of the broad peak at $1300\ \text{cm}^{-1}$ decreases when temperature decreases to 10 K but the peak position almost does not move.

For fcc Ni, besides a Drude response, there are only two broad peaks centering at about 0.3 and $1.4\ \text{eV}$ in the frequency below $4.0\ \text{eV}$ at 300 K.¹⁷ In the ferromagnetic state below the Curie temperature, the exchange interaction lowers the energy of the spin-up electrons and raises the energy of the spin-down electrons of the d bands. This leads to two subsets of electrons in the region of the Brillouin zone surrounding the L point. The $0.3\ \text{eV}$ peak in pure fcc Ni is due to the interband transition between the spin-down electrons of the $3d$ band and the $4s$ band at the Fermi surface. The $1.4\ \text{eV}$ is related to the interband transition from the spin-up band of $3d$ electrons to the $4s$ band at the Fermi level. For MgCNi_3 , there are four broad peaks centering at about 0.16 , 0.71 , 1.59 , and $2.84\ \text{eV}$, respectively. We notice that both the 0.3 and $1.4\ \text{eV}$ peaks in pure fcc Ni disappear in MgCNi_3 . Instead, the number of peaks below $4.0\ \text{eV}$ has increased to four. Considering the small Stoner factor^{7,13} and the dc susceptibility,¹⁰ the four peaks must have a different origin as those observed in the optical conductivity spectra of pure fcc Ni.

According to the theoretical analysis for MgCNi_3 ,^{8,16} Ni $3d$ bands decompose into xy , $yz+zx$, x^2-y^2 , and $3z^2-r^2$ four components in a local tetragonal crystal field.^{8,16} The energy range of band Ni $3d_{xy}$ is $-4.0\sim-0.5\ \text{eV}$. Its main DOS peaks are at about $-1.0\sim-1.3\ \text{eV}$ with a weaker peak at $-2.7\ \text{eV}$. The band Ni $3d_{yz+zx}$ extends in the energy region from -4 to $+1\ \text{eV}$ with two high DOS peaks at about -2.5 and $-0.08\ \text{eV}$, respectively. Ni $3d_{x^2-y^2}$ has some DOS from -4 and $0\ \text{eV}$ with the highest peak at about $-1.7\ \text{eV}$. Band Ni $3d_{3z^2-r^2}$ locates in the range of -4 to $0\ \text{eV}$. It also contributes to the states very close to the Fermi level. The $C\ 2p$ bands hybridize with Ni $3d$ bands. Its main DOS is in the energy range of -7.0 to $-4.0\ \text{eV}$, although $c\ 2p$ bands offer a few DOS near E_F from about -0.1 to $+1\ \text{eV}$ as well. The three peaks in the energy range of 0.5 to $4\ \text{eV}$ observed in Fig. 2 could be attributed to the interband transitions from the occupied Ni $3d$ states to the unoccupied part of the Ni $3d$ state (the major contribution is Ni $3d_{yz+zx}$ bands) which hybridized strongly with the $C\ 2p$ states.¹⁹ The peak of $2.84\ \text{eV}$ can be assigned mainly to the interband transition from the occupied Ni $3d_{yz+zx}$ bands to another unfilled part of the d band with a mixture of unoccupied $C\ 2p$ band, while the $-2.7\ \text{eV}$ DOS peak of Ni $3d_{xy}$ may offer small spectra weight too. The $1.59\ \text{eV}$ peak may be dominated by the interband transition from the occupied $-1.3\ \text{eV}$ peak of Ni $3d_{xy}$ bands to the unoccupied Ni $3d_{yz+zx}/C\ 2p$ mixing states, while the peak of $0.71\ \text{eV}$ may be mainly due to the interband transition from Ni $3d_{3z^2-r^2}$ band to the unoccupied Ni $3d_{yz+zx}/C\ 2p$ mixing

TABLE I. Fitting parameters of Drude and Lorentz components for the conductivity spectra of MgCNi_3 at 300, 180, and 10 K.

T (K)	ω_p	γ	$\omega_{p,1}$	γ_1	ω_0
300	17000	210	41700	5700	1300
180	16300	170	39300	5600	1300
10	16100	98	41200	6000	1300

states. The three peaks of 0.71 , 1.59 , and $2.84\ \text{eV}$ in the experiment is quite consistent with the previous theoretical calculation based on the first principles band structure study.¹⁶ The calculations indicate three peaks at about 0.73 , 1.8 , and $2.9\ \text{eV}$ in the real part of conductivity $\sigma_1(\omega)$ in the region from 0.5 to $4\ \text{eV}$.

The fourth broad peak in our optical conductivity spectra at about $1300\ \text{cm}^{-1}$ has not been discussed in theoretical study.¹⁶ As we describe above, this peak shows a slight temperature dependence. When the temperature decreases, the weight of the peak decreases but the peak position does not move. We find that the sum of one Drude component and one Lorentz component could fit the data at different temperatures below $4000\ \text{cm}^{-1}$

$$\sigma_1(\omega) = \frac{\omega_p^2 \gamma}{4\pi(\omega^2 + \gamma^2)} + \frac{\omega_{p,1}^2 \omega^2 \gamma_1}{4\pi(\omega^2 - \omega_0^2)^2 + \gamma_1^2 \omega^2}, \quad (1)$$

where ω_p is the characteristic plasma frequency of free carriers, $\omega_{p,1}$ is the strength of the bounded carriers associated with the Lorentz component, γ is the inverse of lifetime ($1/\tau$), and γ_1 is the damping coefficient of the Lorentz component. The inset of Fig. 3 shows the fitting result at 10 K. The fitting parameters are listed in Table I.

As we know, the Drude component is due to the intraband transition of conducting carriers. It is mainly contributed by the electrons of Ni $3d_{yz+zx}$ and Ni $3d_{3z^2-r^2}$ bands, which are hybridized strongly with $C\ 2p$ bands and cross the Fermi level. Then, the major concern here is the assignment of the Lorentz component. Because of the substantial Ni-C covalent interaction, the electron-phonon coupling is expected to be strong in this compound,^{8,16} which could lead to polaronic characteristic of charge carriers. On this basis, one may link the broad component to the photoionization effect of polarons. However, the difficulty of this interpretation is that the temperature dependence of the spectral weight of the component is not consistent with the expected behavior of polarons. The peak strength should increase with decreasing temperature for polaronic absorption,²⁰ but in the present compound, the peak spectral weight slightly decreases with decreasing temperature. An alternative explanation is that this electronic band also originates from an interband transition. Since the energy scale of the transition, $1300\ \text{cm}^{-1}$ ($0.16\ \text{eV}$), is quite small, by looking at the calculated band structure along different symmetry lines in the Brillouin zone,^{8,16} we found the transition between the two bands close to the half way along the Γ - M line possible. This is likely corresponding to the transition from the states of the Ni $3d_{3z^2-r^2}$ band just below the Fermi level to the unoccupied

part of the Ni $3d_{yz+zx}$ band hybridized with the C $2p$ band.

It deserves to remark that the plasma frequency ω_p of the Drude term listed in Table I is only about $17\,000\text{ cm}^{-1}$, which is much smaller than the calculated value.¹⁶ We stress that this plasma frequency is different from that deduced by integrating the optical conductivity spectrum $[\sigma_1(\omega)]$ from zero frequency to a cutoff frequency ω_c , which usually is taken at the reflectance edge or minimum position of $R(\omega)$. Obviously, in the later case, it overestimates the plasma frequency because of the inclusion of four interband excitations.

In summary, in this paper we report the experimental measurement of the reflectance spectra $R(\omega)$ and the deduced

frequency dependence of the optical conductivity of MgCNi_3 . Our experimental data and analysis show that Ni $3d$ states really dominate the DOS below 4 eV. The contributions of the free carriers and interband transitions to the conductivity spectra are discussed on the basis of band structure calculations. There is a good agreement between our experimental data and the previous theoretical calculations.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation of China and the Knowledge Innovation Project of the Chinese Academy of Sciences.

*Email address: nlwang@aphy.iphy.ac.cn

- ¹T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. S. Slusky, K. Inumara, H. W. Zandbergen, N. P. Ong, and R. J. Cava, *Nature (London)* **411**, 54 (2001).
- ²S. Y. Li, R. Fan, X. H. Chen, C. H. Wang, W. Q. Mo, K. Q. Ruan, Y. M. Xiong, X. G. Luo, H. T. Zhang, L. Li, Z. Sun, and L. Z. Cao, *Phys. Rev. B* **64**, 132505 (2001).
- ³S. Y. Li, W. Q. Mo, M. Yu, W. H. Zheng, C. H. Wang, Y. M. Xiong, R. Fan, H. S. Yang, B. M. Wu, L. Z. Cao, and X. H. Chen, *Phys. Rev. B* **65**, 064534 (2002).
- ⁴P. M. Singer, T. Imai, T. He, M. A. Hayward, and R. J. Cava, *Phys. Rev. Lett.* **87**, 257601 (2001).
- ⁵J.-Y. Lin, P. L. Ho, H. L. Huang, P. H. Lin, Y.-L. Zhang, R.-C. Yu, C.-Q. Jin, and H. D. Yang, *Phys. Rev. B* **67**, 052501 (2003).
- ⁶A. Szajek, *J. Phys.: Condens. Matter* **13**, L595 (2001).
- ⁷S. B. Dugdale and T. Jarlborg, *Phys. Rev. B* **64**, 100508 (2001).
- ⁸D. J. Singh and I. I. Mazin, *Phys. Rev. B* **64**, 140507 (2001).
- ⁹I. G. Kim, J. I. Lee, and A. J. Freeman, *Phys. Rev. B* **65**, 064525 (2002).
- ¹⁰A. Das and R. K. Kremer, *Phys. Rev. B* **68**, 064503 (2003).
- ¹¹M. A. Hayward, M. K. Haas, A. P. Ramirez, T. He, K. A. Regan, N. Rogado, K. Inumaru, and R. J. Cava, *Solid State Commun.* **119**, 491 (2001).
- ¹²T. G. Kumary, J. Janaki, A. Mani, S. M. Jaya, V. S. Sastry, Y. Hanharan, T. S. Radhakrishnan, and M. C. Valsakumar, *Phys. Rev. B* **66**, 064510 (2002).
- ¹³J. H. Shim, S. K. Kwon, and B. I. Min, *Phys. Rev. B* **64**, 180510 (2001).
- ¹⁴A. Walte, G. Fuchs, K.-H. Muller, A. Handstein, K. Nenkov, V. N. Narozhnyi, S.-L. Drechsler, S. Shulga, L. Schultz, and H. Rosner, *Phys. Rev. B* **70**, 174503 (2004).
- ¹⁵C. M. I. Okoye, *J. Phys.: Condens. Matter* **15**, 833 (2003).
- ¹⁶M. Q. Tan, X. M. Tao, X. J. Xu, J. H. He, and G. X. Ye, *Physica B* **337**, 95 (2003).
- ¹⁷H. Ehrenreich, H. R. Philipp, and D. J. Olechna, *Phys. Rev.* **131**, 2469 (1963), and references therein.
- ¹⁸C. Q. Jin, Y. L. Zhang, Z. X. Liu, F. Y. Li, W. Yu, and R. C. Yu, *Physica C* **388-389**, 561 (2003).
- ¹⁹Generally speaking, the d - d transition is not allowed. However, in solids, because of the hybridizations between the d bands and some other bands from other atoms, the d - d interband transition is usually observed in optical spectra.
- ²⁰S. Yoon, H. L. Liu, G. Schollerer, S. L. Cooper, P. D. Han, D. A. Payne, S. W. Cheong, and Z. Fisk, *Phys. Rev. B* **58**, 2795 (1998).